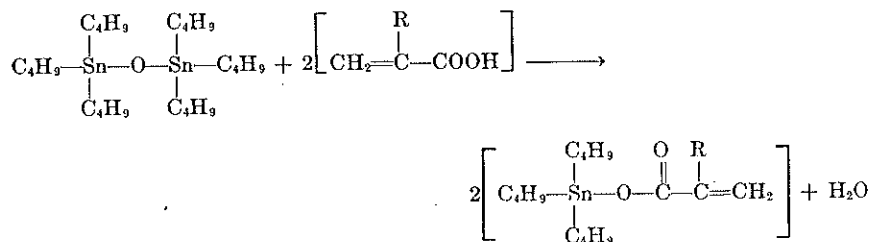


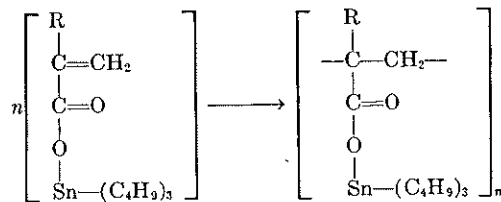
### *Polymers of Tributyltin Acrylate Esters\**

The work reported in this paper is done under a continuing broad program of the Quartermaster Corps, Department of the Army, to develop organometallic elastomers having thermally stable and chemically resistant properties. There is a considerable amount of experimental technical literature<sup>1-3</sup> relating to organometallic derivatives and the possibility of forming polymeric products. Of the many organometallic products reported, only the organosilicon derivatives have been developed to provide elastomeric products of extensive general significance. In many respects these conform in their reactions and structures to the corresponding carbon derivatives. Of the other metals under Group IV of the Periodic Table, titanium, zirconium, and especially tin react similarly in many respects to silicon and to carbon. In its resemblance to silicon, tin appears to have favorable possibilities for varied types of chemical reactions and polymer formation. Unlike silicon and carbon reaction products, however, the dialkyl and diaryl derivatives of tin oxides are insoluble, infusible, polymeric compounds. On the other hand, the properties of alkoxy and dicarboxylic acid derivatives of tin are similar in many respects to the corresponding silicon and carbon compounds.

In the early study of tin reactions, it was found and reported<sup>4</sup> that dibutyltin oxide or diacetate reacted readily with dicarboxylic acids to form either cyclic or chain polymers of varying molecular weights up to 3000. The present discussion deals only with the reactions of tributyltin oxide and acrylic-type monocarboxylic acids. Both methacrylic acid and acrylic acid react readily in 1:1 ratio with the monofunctional tin to form crystalline monomer derivatives. The synthesis of the monomers is schematically shown in the following reaction (where R = H in acrylic acid and CH<sub>3</sub> in methacrylic acid):



The experimental details will be discussed later. These monomers may be polymerized either by solution (using benzene) or water emulsion-type polymerization into rubbery or elastomeric products. Polymerization is accomplished according to the following reaction:



The product is a typical chain-type vinyl polymer with carbon to carbon connecting links. The carboxyl-tin chain is attached in pendant position to the polymer chain.

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## EXPERIMENTAL

## I. Monomer Synthesis

## A. Methacrylic Acid Ester of Tributyltin Oxide

To 103.8 g. tributyltin oxide in 300 ml. benzene in a flask equipped with stirrer and reflux condenser 30 g. methacrylic acid was added slowly. Cooling was employed to prevent a rise in temperature. The temperature was not allowed to rise above 25°C. during the acid addition. After all the acid was added, the solution was heated gradually and maintained at 30°C. At the same time vacuum was applied to remove the water of reaction. The benzene loss during this period was replaced by the addition of benzene through a dropping funnel. When the solution became clear, heating was continued for one more hour and all the benzene evacuated. The total reaction time was 5 hours. The resulting pale yellow viscous liquid was then diluted with 100 ml. petroleum ether and cooled to -20°C. The product separated as long, thick, transparent crystals, having a m.p. of 18°C. The yield approaches the theoretical. This monomer is the methacrylic acid ester of tributyltin oxide which was used in subsequent polymerizations either by the solution or emulsion system.

Anal. Calcd. for  $C_{16}H_{32}O_2Sn$ : Sn, 31.7%. Found: Sn, 30.7.

## B. Acrylic Acid Ester of Tributyltin Oxide

To 103.8 g. tributyltin oxide in 300 ml. benzene in a flask equipped with stirrer and reflux condenser 25.1 g. acrylic acid was added slowly. After 20 minutes standing, the solution was heated at 50°C. for 1 hour and then refluxed for 3½ hours. The benzene was evaporated and the remaining product heated at 112°C. for 2 hours. The resulting viscous liquid was then purified by solution and crystallization in petroleum ether. The transparent monomer crystals have a melting point of 74.5-75°C. The yield is practically 100%.

Anal. Calcd. for  $C_{15}H_{30}O_2Sn$ : Sn, 32.9%. Found: Sn, 32.6%.

## II. Polymerization

## A. Methacrylic Acid Ester of Tributyltin Oxide

1. **Solution-type polymerization.** a. Benzoyl peroxide as catalyst. The monomer in crystalline form obtained in IA was dissolved in 80 ml. benzene. To this solution 1% by weight of benzoyl peroxide based on the monomer used was added in increments. After standing for 15 minutes to initiate the reaction, the benzene solution was heated in a covered beaker at light reflux on a hot water bath for 3 hours. The benzene was then evaporated on the hot water bath and finally in a vacuum oven at 110°C. for 3 hours. When cooled the resulting elastomer is a tough, semisolid material with characteristic rubber properties. The yield is approximately 98%.

b. Dicumyl peroxide as catalyst. The procedure in (a) was repeated except that dicumyl peroxide was used instead of benzoyl peroxide. This resulted in a somewhat harder and tougher elastomer, having a high tensile strength. It could be removed from the beaker only with difficulty.

2. **Emulsion-type polymerization.** The monomer in crystalline form obtained in IA was polymerized by emulsion polymerization procedure using the conventional mercaptan-persulfate catalyst according to the following formulation:

Monomer	100
Water	180
Tergitol NPX (non-ionic)	5
Lauryl mercaptan	0.5
Potassium persulfate	0.3

The monomer was added slowly (in small increments) to the catalyst solution in a flask equipped with electric stirrer. The polymerization continued at 50°C. with constant stirring for 9 hours. The latex was then removed from the reaction flask. The polymer was coagulated with alcohol. The precipitate was well washed and then dried for 48 hours at 50°C. under vacuum. The resulting product is slightly yellow, tough rubbery material. The yield is 80% of theoretical.

*B. Acrylic Acid Ester of Tributyltin Oxide*

**1. Solution-type polymerization.** *a.* Benzoyl peroxide as catalyst. The monomer in crystal form obtained in IB was dissolved in 50 ml. benzene. To this solution 1% by weight of benzoyl peroxide based on the monomer used was added slowly. After being heated 2 hours at reflux, an additional 3% benzoyl peroxide was added and heating continued at 125–130°C. for 14 hours. The resulting product was a very viscous, light-colored oil.

The above was repeated except that 2% benzoyl peroxide was used at the start instead of 1% and the reflux at 78°C. was continued for 10 hours instead of 2 hours. Additional 2% benzoyl peroxide was added after refluxing. The heating was continued at 140°C. for 12 hours. The resulting product was a rubbery material but softer and less tough than those obtained with methacrylic acid.

*b.* Dicumyl peroxide as catalyst. The monomer obtained in IB was dissolved in benzene. To this solution 1% benzoyl peroxide based on the monomer used was added. The reaction continued for 1 hour at 140°C. On cooling a soft, flexible, slightly elastomeric material was obtained resembling the one obtained when using benzoyl peroxide as catalyst.

The procedure in 1(a) was repeated except that 2% dicumyl peroxide instead of benzoyl peroxide was added at the start. The refluxing continued for 10 hours. After refluxing, an additional 2% dicumyl peroxide was added. The heating was continued at 140°C. for 12 more hours. A soft elastomeric material was obtained upon cooling.

**2. Emulsion-type polymerization.** The monomer in crystalline form obtained in IB was polymerized by emulsion polymerization procedure using the same conventional lauryl-mercaptan-potassium persulfate system as in A(2). Polymerization was at 50°C. for 9 hours. The latex was coagulated with alcohol. The resulting product is rubbery but not so tough and elastic as that obtained with methacrylic acid. The yield is 75–80%.

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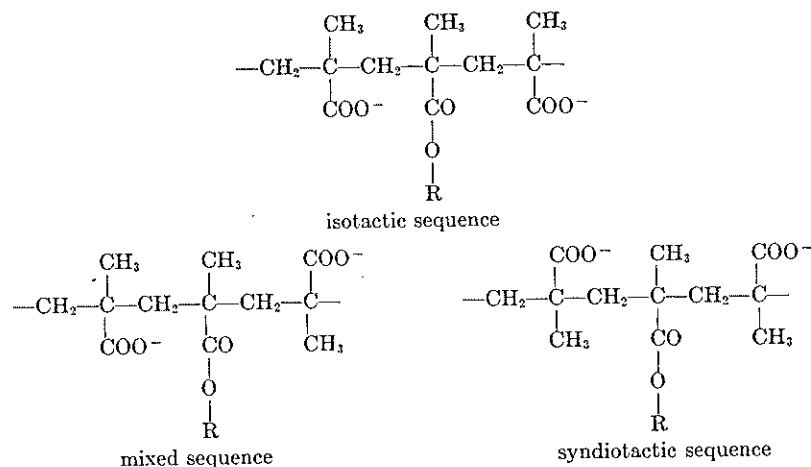
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### A Kinetic Approach to the Characterization of the "Microtacticity" of a Polymer Chain

A great deal of investigation on stereospecific polymerization carried out in recent years has been severely handicapped by the fact that only crystallographic methods could be used to characterize the steric configuration of the polymer chains. These methods lend themselves only to the study of polymers containing long sequences in which the asymmetric carbon atoms have either identical, (isotactic) or regularly alternating (syndiotactic) configurations. For polymers in which the distribution of the configurations of the asymmetric centers deviates only relatively little from randomness, no experimental method for the characterization of such distributions (the "microtacticity" of the polymer) was available.

We believe to have evidence that kinetic studies of reactions involving two groups attached to neighboring asymmetric carbon atoms along the polymer chain may make an important contribution to this problem. A convenient reaction for such studies is the solvolysis of a phenyl ester group whose rate is governed, under certain conditions, by the attack of a suitably spaced neighboring ionized carboxyl group.<sup>1</sup>

Zimmering observed some years ago<sup>2</sup> that the solvolysis of copolymers of methacrylic acid containing 1-2% *p*-nitrophenyl methacrylate did not follow first-order kinetics, but that the polymer behaved as if part of the ester groups were very much more reactive than the remainder. We believe now that this behavior reflects differences in the stereochemical arrangements in the immediate neighborhood of the ester group:



We have followed by UV spectroscopy the hydrolysis of methacrylic acid copolymers containing 1.8 mole-% *p*-nitrophenyl methacrylate (NPM) or 3.0 mole-% *p*-methoxyphenyl methacrylate (MPM). These monomers were found to copolymerize almost at random, so that with the low ester content practically all ester groups were flanked by two methacrylic acid units. A typical plot of  $\log (E/E_0)$  against time ( $E$  and  $E_0$  being the instantaneous and initial ester concentrations, respectively) is given in Figure 1. The dashed extrapolation of the experimental curve represents the contribution of the "slow" ester groups to the reaction. The experimental data could in all cases be accounted for by a kinetic scheme of the type

$$(E/E_0) = \alpha \exp\{-k_1 t\} + (1 - \alpha) \exp\{-k_2 t\} \quad (1)$$

where  $\alpha$  is the fraction of "fast ester" groups, while  $k_1$  and  $k_2$  are first-order rate constants for the reaction of "fast" and "slow" groups, respectively. The results for the parameters